

..... Teixeira, Pereira, Nakamura, Brum: Adhesivity of Bio-Based Anhydrous Citric Acid...

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Adhesivity of Bio-Based Anhydrous Citric Acid, Tannin-Citric Acid and Ricinoleic Acid in the Properties of Formaldehyde-Free Medium Density Particleboard (MDP)

Mogućnost primjene ekološki prihvatljivoga anhidrida limunske kiseline, taninsko-limunske kiseline i ricinoleinske kiseline kao ljepila za proizvodnju iverica srednje gustoće (MDP) bez formaldehida

Original scientific paper • Izvorni znanstveni rad

Received – prispjelo: 12. 3. 2019.

Accepted – prihvaćeno: 28. 4. 2020.

UDK: 630*863.21

<https://doi.org/10.5552/drvind.2020.1917>

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ABSTRACT • Particles of flooded gum (*Eucalyptus grandis*) were bonded using three bio-based adhesives - anhydrous citric acid (CA), tannin-citric acid (TCA) and ricinoleic acid (RA) - from renewable sources and hot pressed to produce medium density particleboard (MDP). The bonding capacity of such adhesives and properties of the MDP were evaluated and compared to the requirements of seven grades of particleboards, according to the EN 312 (2010) standard. The RA did not create adhesion reaction with the wood particles. Adhesives formulated with CA and TCA presented capacity to bond eucalyptus particles into MDP confirmed by esterification reactions of the FTIRS analysis. MDP bonded with CA met requirements as high as grade P5 of the EN 312 (2010) standard for static modulus of elasticity (MOE) and internal bond (IB) and P2 for modulus of rupture (MOR). Panels bonded with TCA met requirements up to grade P3 for MOE, however, did not withstand water absorption.

Keywords: *Eucalyptus grandis*; bio-based adhesives; particleboards; bonding capacity; FTIR analysis; EN requirements

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SAŽETAK • Za izradu iverice srednje gustoće (MDP) upotrijebljeno je iverje drva eukalipta (*Eucalyptus grandis*) lijepljeno trima ekološki prihvatljivim ljepilima dobivenim iz obnovljivih izvora na bazi anhidrida limunske kiseline (CA), taninsko-limunske kiseline (TCA) i ricinoleinske kiseline (RA) te prešano u vrućoj preši. Kvaliteta lijepljenja tim ljepilima i svojstva iverice ocijenjeni su usporedbom sa sedam klasa uporabe prema normi EN 312 (2010). Ljepilo RA nije uspjelo povezati drveno iverje. Ljepila CA i TCA pokazala su sposobnost lijepljenja eukaliptova iverja pri izradi MDP ploče, što je potvrđeno reakcijom esterifikacije u FTIR analizi. MDP ploča izrađena primjenom CA ljepila udovoljava visokim zahtjevima klase uporabe P5 prema EN 312 (2010) za modul elastičnosti (MOE) i čvrstoću na raslojavanje (IB) te klase P2 za modul loma (MOR). Ploče izrađene uporabom TCA ljepila ispunile su zahtjeve klase uporabe P3 za modul elastičnosti (MOE), ali nisu zadovoljile zahtjeve o upijanju vode.

Ključne riječi: *Eucalyptus grandis*; ekološki prihvatljiva ljepila; iverice; sposobnost lijepljenja, FTIR analiza, EN zahtjevi

1 INTRODUCTION

1. UVOD

Medium Density Fiberboard (MDF), Hardboard or fiberboard (HB) and High Density Fiberboard (HDF) are reconstituted wood-based panels composed of wood fibers, while Medium Density Particleboard (MDP) is produced with wood particles and adhesive, pressed under high pressure and temperature. MDF and HDF are produced with the addition of a synthetic adhesive using a dry process and their density ranges from 600 to 900 kg/m³, and HB results from hot pressing that uses a wet process without the addition of adhesives that reactivates the natural binders of wood, such as lignin.

MDP is a popular composite with density ranging from 551 to 750 kg/m³, which presents high use of wood raw material, mainly from planted forests, at affordable price, with broad application in the furniture industry, construction/remodeling and handmade articles in replacement of solid wood (FAO, 2017).

MDP and MDF are currently the most consumed wood-based reconstituted panels worldwide (FAO, 2017). The Brazilian production of reconstituted wood-based panels in 2018 was 8.2 million m³, 40 % MDP and 60 % MDF/HDF. The production of MDF/HDF and HB dropped 2.5 % and 0.4 %, respectively; MDP increased 3.4 % (IBÁ, 2019).

The Brazilian wood-based panel sector ranked 8th place in 2018 in the global market of largest producers, the same position as the previous year (IBÁ, 2019).

Formaldehyde-based synthetic resins are the most used adhesives in the production of reconstituted wood-based panels, especially urea-, phenol- and melamine-formaldehyde, and the combination of these resins. The formaldehyde acts as the catalyst of the resin setting.

According to Silva *et al.* (2013), the urea-formaldehyde adhesive is the most significant input to environmental impacts of reconstituted panels, such as abiotic resources depletion, eutrophication, ozone photochemical formation, acidification and global warming. Furthermore, chemical compounds based on formaldehyde are classified by the International Agency for Research on Cancer (IARC) as carcinogenic, tumorigenic and teratogenic. According to IARC (2006), historically, the major source of formaldehyde gas release in dwellings is urea-formaldehyde derived from insulation panels. That is why the replacement of

formaldehyde-based adhesives is currently in demand and requires research into developing new and sustainable adhesives, especially bio-based ones that should be biodegradable, non-polluting, derived from renewable sources and economically feasible.

In this context, previous publications on the use of citric acid as a bio-based adhesive in MDP have presented promising results (Umemura *et al.*, 2012a, b, 2013; Liao *et al.*, 2016; Kusumah *et al.*, 2016). Although the adhesion mechanism with citric acid is yet not well known, acts as a cross-linking agent, forming ester bonds with wood biopolymers (Yang *et al.*, 1996; Zagar and Grdadolnik 2003; Umemura *et al.*, 2013, 2015; Widyorini *et al.*, 2016; Kusumah *et al.*, 2016).

Tannins are also an alternative for formaldehyde-based resins, due to the large number of phenolic rings in its structure (Santana and Teixeira, 1996; Chupin *et al.*, 2013). Zhao *et al.* (2015) investigated the effects of citric acid on the curing properties of tannin-sucrose adhesives and concluded that the addition of citric acid promotes the reaction between tannin and sucrose at lower temperatures. Ricinoleic acid is also from a renewable source, derived from castor bean oil, which could be used to form polyesters (Péres *et al.*, 2014) and, probably, be used as a natural adhesive in particleboards.

Environmental and human health benefits are the main advantage of these three compounds, as they are formaldehyde-free, non-toxic and non-polluting substances. They are also derived from renewable resources and can generate biodegradable materials. Consequently, the application of such materials in the industry can reduce the environmental impact and minimize the demand for petroleum products.

Considering the above, the present work aims at evaluating the properties of MDP made with eucalyptus particles bonded with three bio-based adhesives based on ricinoleic acid, anhydrous citric acid and tannin-citric acid.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Particles processing

2.1. Proizvodnja iverja

Eucalyptus grandis flakes were hammer-milled and classified into particles after passing through a set of screen sieves. Then, particles were classified in a

vibrating sieve by a set of sieves of 20, 40 and 60 mesh. Particles retained in the 40 mesh sieve were used in the panels production.

In order to evaluate if the proposed pressing temperature of MDPs was adequate, thermal analysis of the particles was performed using a thermogravimetric analyzer Shimadzu, model DTG-60H at a heating rate of 10 °C/min from 25 °C to 800 °C with nitrogen flow of 30 mL/min.

2.2 Preparation of adhesive solutions

2.2. Priprema ljepila

For the manufacture of the medium density particleboard, three formulations of adhesives were used: anhydrous citric acid (CA), tannin-citric acid (TCA) and ricinoleic acid (RA).

Anhydrous Citric Acid (CA) at 99.5 % purity level was purchased from food suppliers. The CA adhesive formulation was prepared by mixing water and CA at a ratio of 1:1 (mass:mass). The viscosity of the solution was measured in a rotational Brookfield DV-I-Prime viscometer for small samples using #18 spindle, at the speed of 100 RPM and room temperature of (27±2) °C. A pH indicator tape was used to measure the solution pH. The CA formulation presented pH of 1 and viscosity of 74 cP.

For the preparation of the ricinoleic acid (RA), castor bean oil was saponified with NaOH solution, followed by acidification with HCl, according to the methodology used by Péres *et al.* (2014).

The tannin-citric acid adhesive (TCA) was prepared as an aqueous solution by dissolving citric acid and tannin in water. Initially, the tannin was diluted in water at a ratio 1:1 (mass:mass) at 50°C until complete solubilization, and then the citric acid was added at the same ratio.

2.3 Manufacture of MDPs

2.3. Izrada MDP ploča

The adhesive solutions were sprayed onto selected particles (-40 mesh +60 mesh) in a rotatory drum mixer, and the furnish was subsequently dried at 60 °C, for 6 hours, to 9 % moisture content (determined in a moisture meter thermobalance model BEL). The mat was hand formed and hot pressed at (180 ± 3) °C for 10 minutes under the pressure of 4 MPa. Single-layer flat boards were produced with dimensions of 30 cm (length) × 30 cm (width) × 1 (thickness) cm. The three adhesive solutions (CA, TCA and RA), as described above, were tested at a concentration of 18 % based on the dry mass of particles (Table 1).

For each treatment, three panels were produced, from which five specimens were cut for each test. The

panels were conditioned in a climate room with controlled conditions of relative humidity (60±2) % and temperature (20±1) °C to reach equilibrium moisture content.

2.4 MDP characterization

2.4. Karakterizacija MDP ploča

The physical properties evaluated were density (EN 323:1993), water absorption (*WA*) and thickness swelling (*TS*) after 24 hours immersion in water (EN 317:1993). For the evaluation of mechanical properties, the internal bonding (*IB*) (EN 319:1993), modulus of elasticity (*MOE*) and modulus of rupture (*MOR*) in static bending (EN 310:1993) were determined. The panels were classified according to the requirements of EN 312:2010 standard, which establishes seven grades of particleboards.

The experiment was carried out in a completely randomized design (CRD). Statistical analysis was conducted using the t-student test at 5 % significance level.

2.5 Scanning Electron Microscopy (SEM)

2.5. Pretražni elektronski mikroskop (SEM)

Samples of particles and particles detached from panels were analyzed by Scanning Electron Microscopy (SEM), using a Field Emission Electron Microscope (JEOL, JSM-7001 F) operating at 15 kV. For SEM analysis, particles were pre-treated by sputter coating with gold.

2.6 Carbon-Hydrogen-Nitrogen analysis

2.6. Ugljik-vodik-dušik analiza

The Carbon-Hydrogen-Nitrogen (CHN) analyses were carried out in an Elemental Analyzer Perkin Elmer, model EA 2400 Series II, aiming to evaluate the carbon gain (*CG*) that was calculated by equation 1, and expressed as mean values of three measurements:

$$\%CG = \frac{(\%CAP - \%CBP)}{\%CBP} \times 100 \quad (1)$$

Where:

%CG – carbon gain after pressing;

%CAP – carbon content in eucalyptus particles after pressing;

%CBP – carbon content in eucalyptus particles before pressing.

2.7 FTIR analysis

2.7. FTIR analiza

Samples from non-treated particles and from particleboards were ground in a hammer mill and then pelleted in Potassium bromide (KBr). The KBr disks were analyzed by Fourier Transform Infrared (FTIR) spec-

Table 1 Description of MDP manufacturing parameters

Tablica 1. Parametri izrade MDP ploča

Adhesive / Ljepilo	Pressing conditions Uvjeti prešanja	Adhesive Ljepilo, %	ρ^* , g/cm ³
Anhydrous citric acid (CA) / anhidrid limunske kiseline (CA)	180 °C/10 min	18	0.80
Ricinoleic acid (RA) / taninsko-limunska kiselina (TCA)	180 °C/10 min	18	0.80
Tannin-citric acid (TCA) / ricinoleinska kiselina (RA)	180 °C/10 min	9 (CA)/9 (TAN)	0.80

* ρ – target apparent density (at 12 % moisture content) / ρ – ciljana prividna gustoća (pri 12 % sadržaja vode); TAN – tannin / TAN – tanin

troscopy in the mid-infrared spectrum ($4000 - 400 \text{ cm}^{-1}$) using a Shimadzu spectrometer, model IR Prestige-21.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

3.1 DTG analysis

3.1. DTG analiza

The TG and DTG curves of eucalyptus particles indicated three bands of thermal degradation (Figure 1), the first (from 25°C to 89°C) corresponding to approximately 7.13 % of mass loss, was attributed to moisture loss. The two others were attributed to the degradation of hemicellulose and cellulose (from 230°C to 362°C) and lignin deterioration (364°C to 510°C), as lignin is the most resistant biopolymer of lignocellulosic materials (Seye *et al.*, 2010).

In the temperature range of $100\text{--}220^\circ\text{C}$, the mass loss was about 0.82 %. According to Randriamanantena *et al.* (2009), this range corresponds to the zone of thermal stability, which is limited by the initial thermal degradation temperature of the main components of wood. This indicates that the ideal temperature for pressing eucalyptus particleboards should be in between this range.

3.2 SEM analysis

3.2. SEM analiza

Non-treated particles presented apparent pores, which is typical of lignocellulosic materials (Figure 2a), while particles from panels with ricinoleic acid, anhydrous citric acid and tannin-citric acid were covered by the adhesives and presented more heterogeneous surfaces (Figure 2b, c, d). Comparing to other treatments, particles covered by RA (Figure 2b) presented more loose fibril bundles. This analysis is important to under-

stand the ability of the particles to be bonded to the adhesives and how the pores are filled up.

3.3 MDP properties

3.3. Svojstva MDP ploča

Particleboards bonded with RA did not present sufficient adhesion even after being pressed at 180°C for 10 minutes. As a result, it was not possible to characterize RA bonded particleboards. Compared to CA panels, TCA particleboards presented visibly lower adhesion and particles were easily detached and presented rougher surface.

After the water immersion test, the specimens of TCA bonded panels disintegrated into loose particles indicating that the adhesive was not resistant to water. Thus, it was impossible to measure *TS* and *WA*. However, CA particleboards maintained their integrity after immersion in water but they did not achieve the minimum requirements of the EN 312:2010 for *TS*. The resistance of CA particleboards against water can be explained by Vukusic *et al.* (2006), who described the chemical reaction between CA and wood cellulose, in which hydrophobic esters groups replaced some hydrophilic groups of wood biopolymer, reducing the absorption of water by wood particles.

According to Table 2, there is no significant difference in apparent density of CA and TCA treatments. The moisture content of both treatments met the requirements specified by the EN 312:2010 standard.

All mechanical properties (*MOR*, *MOE* and *IB*) of panels bonded with CA were higher than those of panels bonded with TCA, indicating that this treatment presented better adhesion. Taking into account the requirements of EN 312:2010 standard, in general MDPs produced with anhydrous citric acid are graded as panels to be used in dry conditions (P2 boards). Neverthe-

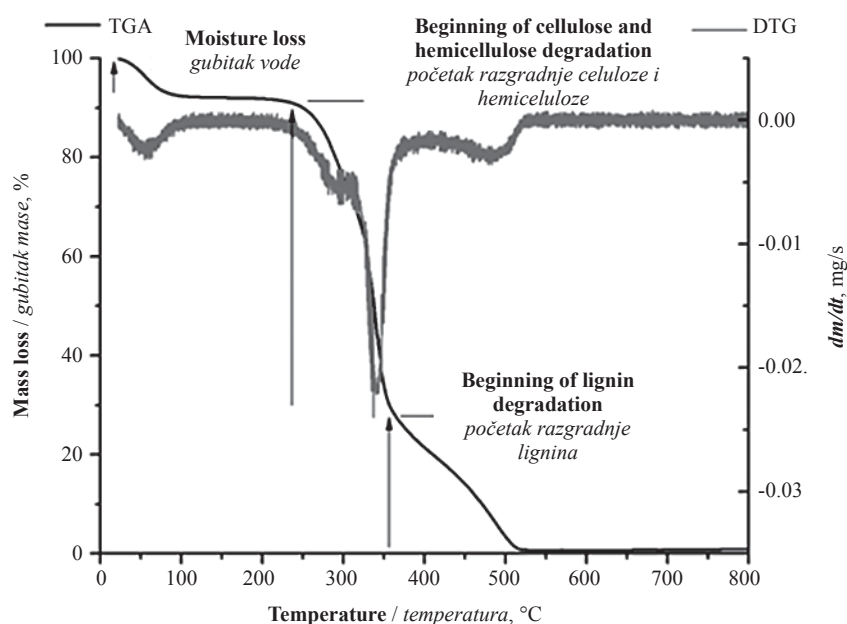


Figure 1 Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curve of eucalyptus particles “in natura”

Slika 1. Termogravimetrijska analiza (TGA) i derivirana termogravimetrijska (DTG) krivulja iverja prirodnog drva eukalipta

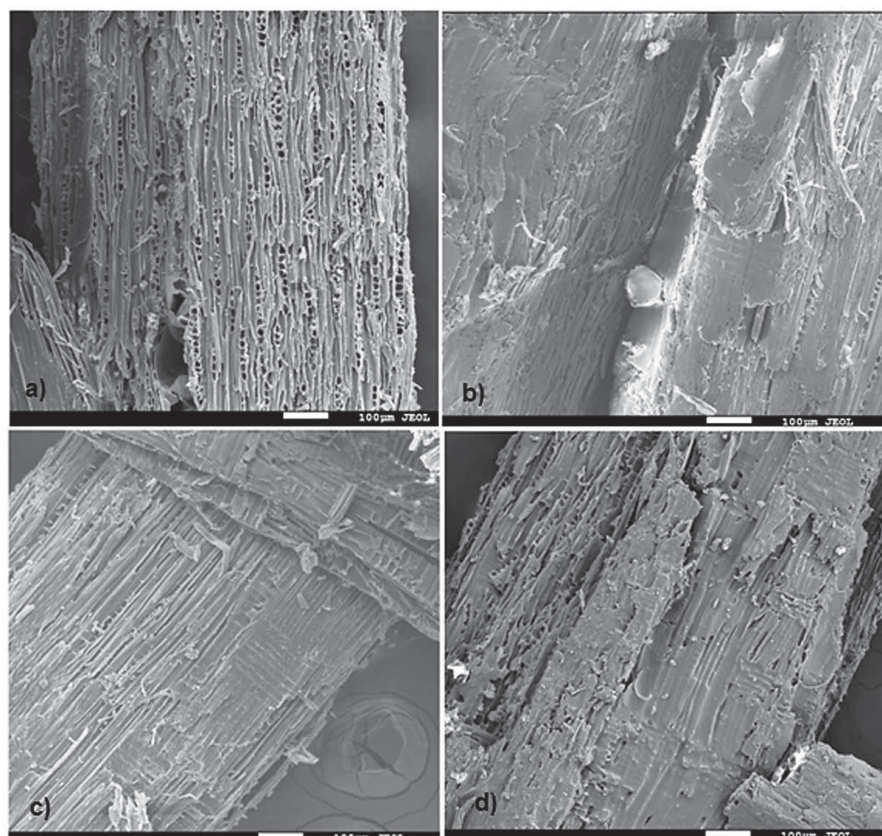


Figure 2 Micrographs of particles detached from panels after pressing. a) eucalyptus particle (“in natura”); b) eucalyptus particle with ricinoleic acid resin; c) eucalyptus particle with anhydrous citric acid resin; d) eucalyptus particle with tannin-citric acid resin

Slika 2. Mikrofotografije iverja odvojenoga iz ploča nakon prešanja: a) iverje drva eukalipta (prirodno); b) iverje drva eukalipta sa smolom ricinoleinske kiseline; c) iverje drva eukalipta sa smolom anhidrida limunske kiseline; d) iverje drva eukalipta sa smolom taninsko-limunske kiseline

less, considering only mechanical properties (*MOR*, *MOE* and *IB*), they were graded as load bearing boards to be used in humid conditions (P5 boards). As for the panels bonded with tannin-citric acid they did not meet the minimum requirements for *IB* and *MOR*, while the requirements of non-load bearing boards were met for *MOE*.

The temperature and pressure applied in CA particleboards were sufficient to promote polymerization re-

actions between the citric acid molecules and wood molecules. It is likely that, due to polyesterification reactions, the adhesiveness was between carboxylic groups of citric acid and the hydroxyl groups of wood biopolymers (lignin, cellulose and hemicellulose) (Figure 3). According to Mano and Mendes (1999), molecules with functional groups that are prone to reactions by three or more points, which is the case of citric acid, may create cross-linked polymers with thermosetting characteristics.

Table 2 Means and coefficient of variation of physical and mechanical properties of MDPs

Tablica 2. Srednje vrijednosti i koeficijenti varijacije fizičkih i mehaničkih svojstava MDP ploča

Adhesive <i>Ljepilo</i>	ρ , g/cm ³	Modulus of rupture <i>MOR</i> Modul loma <i>MOR</i> MPa	Modulus of elasticity <i>MOE</i> Modul elastičnosti <i>MOE</i> MPa	Internal bonding <i>IB</i> Čvrstoća na raslojavanje <i>IB</i> MPa	Moisture content <i>MC</i> Sadržaj vode <i>MC</i> %	Thickness swelling <i>TS24h</i> Debljinsko bubrenje <i>TS24h</i> %	Water absorption <i>WA24h</i> Upojnost vode <i>WA24h</i> %
Ricinoleic acid (RA) <i>ricinolenska kiselina (RA)</i>	NA*	NA	NA	NA	NA	NA	NA
Anhydrous citric acid (CA) <i>anhidrid limunske kiseline (CA)</i>	0.80 ^{a**} (5.6)***	12.04 ^b (10.7)	2,823.8 ^b (7.5)	0.49 ^b (16.6)	10.17 ^b (4.1)	22.04 (4.7)	52.8 (8.9)
Tannin-citric acid (TCA) <i>taninsko-limunska kiselina (TCA)</i>	0.80 ^a (6.8)	9.37 ^a (24.0)	2,201.0 ^a (24.7)	0.24 ^a (32.0)	9.27 ^a (2.5)	NA	NA

*NA – not available / *NA – nije dostupno*

**Mean values followed by the same letter in the same column are not significantly different by the *t*-student test at 5 % significance level. / *Ako se iza srednjih vrijednosti u istom stupcu nalazi isto slovo, tada se one ne razlikuju značajno uz razinu značajnosti od 5 % prema t-testu.*

***Numbers in parenthesis are coefficients of variation, %. / *Brojevi u zagradama koeficijenti su varijacije, %.*

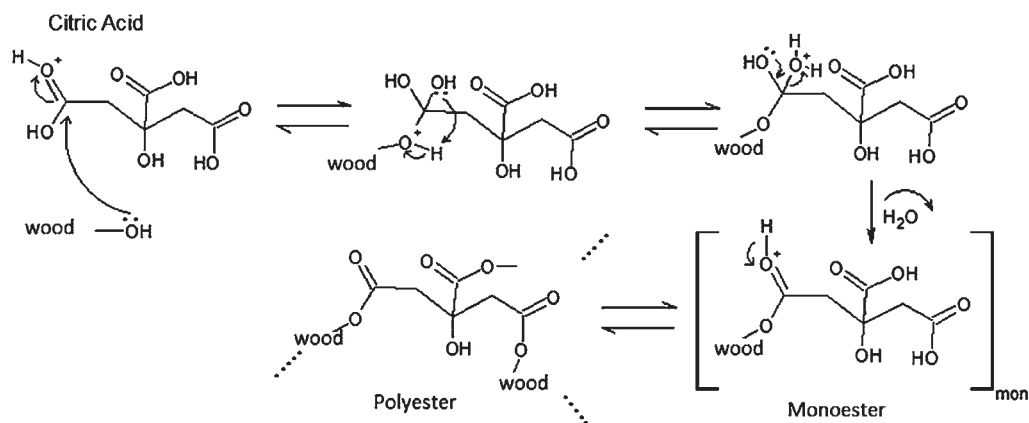


Figure 3 Proposed scheme of polyesterification reaction in anhydrous citric acid bonded particleboards

Slika 3. Predložena shema reakcije poliestifikacije u ivericama izrađenima primjenom ljepljiva na bazi anhidrida limunske kiseline

In particleboards bonded with tannin-citric acid, the most probable adhesion mechanism is also polyesterification between citric acid, tannin and the hydroxyl groups of wood biopolymers. However, it is more likely that reactions between tannin and citric acid molecules took place, since the tannin is more accessible than wood biopolymers. This can explain why samples disintegrated into loose particles after water immersion.

The particles of panels bonded with ricinoleic acid did not create adhesion reaction, even in the presence of two functional groups (carboxyl and hydroxyl) prone to esterification reaction with the hydroxyl sites of wood biopolymers. It may be stated that pressing conditions were not sufficient to promote such esterification reaction. Furthermore, Péres *et al.* (2014) obtained a biopolyester of ricinoleic acid, without catalysts, only after six hours of reaction in a reactor at 190 °C. Additionally, the molecule of ricinoleic acid is larger than that of citric acid, which may hinder the linking process with wood hydroxyls.

3.4 CHN elemental analysis

3.4. Elementarna analiza CHN

The carbon gain (CG) after pressing the particleboard was 0.4 % with CA and 3.91 % with TCA (Table 3). These results are an indicator that esterification reaction took place in the pressed glued particles.

Table 3 Carbon-Hydrogen-Nitrogen analysis of eucalyptus particles

Tablica 3. Ugljik-vodik-dušik analiza iverja drva eukalipta

Particle / Iverje*	%C	%H	%N	%CG**
E	45.80	6.05	0.14	-
CA	46.00	5.92	0.11	0.44
TCA	47.59	6.14	0.18	3.91

*E – untreated eucalyptus particles (“in natura”); CA – eucalyptus particles bonded with anhydrous citric acid; TCA – eucalyptus particles bonded with tannin-citric acid / E – prirodno iverje drva eukalipta; CA – iverje drva eukalipta lijepljeno anhidridom limunske kiseline; TCA – iverje drva eukalipta lijepljeno taninsko-limunskom kiselinom

** CG – carbon gain / dobitak ugljika

3.5 FTIR analysis

3.5. FTIR analiza

The IR spectra of eucalyptus particles “in natura” presented a larger band in the region of 3400 cm⁻¹ (Figure 4a), which indicates the presence of O-H stretch.

The fingerprint region between 1725-1740 cm⁻¹ presented a peak, which is related to axial stretching of carbonyl groups (C=O) in carboxylic acid groups. The 1050 cm⁻¹ band corresponds to stretches of the C-O group of celluloses, hemicelluloses and lignin or to the C-O-C groups of hemicellulose (Brum *et al.*, 2008).

The bands of IR spectra at 1508 cm⁻¹ and 1430 cm⁻¹ are related to the aromatic ring vibrations of the guaiacyl present in lignin (Hergert, 1971). The bands observed below 1000 cm⁻¹ correspond to hydroxyl groups of cellulose (Castro *et al.*, 2004).

Regarding CA bonded particleboards (Figure 4b), peaks of IR spectra were observed in four characteristic bands indicating esterification reactions. The first was a strong and prominent peak in band 1737 cm⁻¹, corresponding to the carbonyl stretching (C=O) of ester. The second was a peak in the band at 1374 cm⁻¹, corresponding to CH bonds of CH₃ groups. The third was a peak in between 1200-1350 cm⁻¹, indicating stretching the C-O bond of -O-(C=O)-. The last peak was in the bands between 1010-1150 cm⁻¹, corresponding to stretches of C-O bonds (Pavia *et al.*, 2008.). There was also a broad band in the region between 3200-3600 cm⁻¹, corresponding to the axial deformation of O-H groups. This can be attributed to the presence of water or to the hydroxyls of wood that were not chemically bonded with the citric acid.

Particleboards bonded with TCA adhesive (Figure 4c) have also shown IR spectra with a broad peak in the band between 3200-3600 cm⁻¹. TCA particleboards presented peaks between bands 1010-1150 cm⁻¹ and in between 1200-1350 cm⁻¹. However, when compared to CA bonded particleboards, there was no evidence of a strong peak at the band 1737 cm⁻¹, indicating less esterification reactions between particles and TCA adhesive.

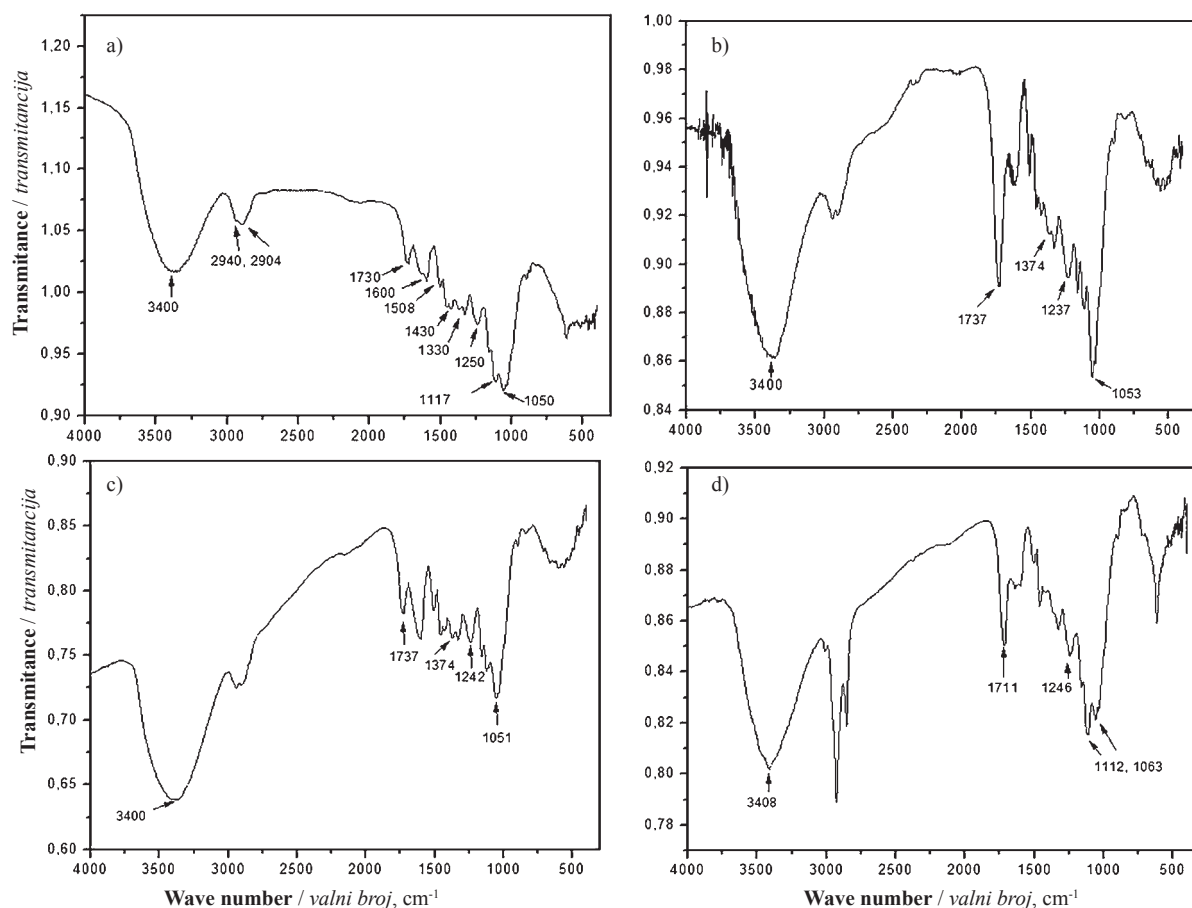


Figure 4 FTIR spectra: a) eucalyptus particles “in natura”; b) CA particleboards; c) TCA particleboards; d) RA particleboards
Slika 4. FTIR spektri: a) prirodno iverje drva eukalipta; b) CA iverice; c) TCA iverice; d) RA iverice

Finally, RA bonded particleboards (Figure 4d) presented a prominent peak in 1711 cm⁻¹ band, which is typical of C=O groups of carboxylic acids. When compared to CA particleboards, RA bonded panels also presented a lower peak in the band 1737 cm⁻¹. These results indicate a little or no esterification reaction that is related to the lack of adhesiveness in RA particleboards.

4 CONCLUSIONS

4. ZAKLJUČAK

The bio-based adhesives formulated with anhydrous citric acid and tannin-citric acid presented the capacity to bond eucalyptus particles into MDPs. Yet, ricinoleic acid cannot be used as an adhesive for particleboards based on the parameters used in this study.

The particleboards with anhydrous citric acid as adhesive presented the best physical and mechanical properties. For *MOR*, the MDPs met the requirements for the use in interior fitments, in dry conditions. For *MOE* and *IB*, it met the requirements for the use of load bearing boards in humid conditions (EN 312, 2010).

The FTIRS analysis confirmed esterification reactions in tannin-citric acid and anhydrous citric acid bonded particles, which is related to the adhesives polymerization, and MDP that met the requirements as high as P3 grade for *MOE*.

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